Table I. Comparison of Total Energies (hartrees) of C_{2v} and C_s Structures at 3-21G Geometries[a]

	RHF/3-21G (6-31G*)	UHF/3-21G (6-31G*)	RMP2/6-31G*	UMP2/6-31G*	$\langle S^2 \rangle$
C_s	−192.792 54 (−193.862 67)	−192.800 72 (−193.87128)	−194.529 32	−194.484 79	0.8
C_{2v}	−192.684 67 (−193.759 08)	−192.793 30 (−193.86410)	−194.401 01	−194.454 01	1.3

[a] MP2 calculations with frozen core. $\langle S^2 \rangle$ values from UHF/6-31G* calculations.

Table II. Comparison of Energies (kcal/mol) of C_{2v} and C_s Structures (3-21G) Relative to (*Z*)-1,3-Pentadiene

	RHF/3-21G (6-31G*)	UHF/3-21G (6-31G*)	RMP2/ 6-31G*	UMP2/ 6-31G*
C_s	54.8 (58.7)	49.6 (53.6)	37.6	65.5
C_{2v}	122.5 (123.8)	54.3 (57.8)	118.1	84.8

Table III. Total Energies and Activation Energies for the 1,5-Sigmatropic Shift

computational level	$-E_{TS}$, hartree	ΔE, kcal/mol
RHF/STO-3G	191.501 70	64.3
RHF/3-21G	192.792 54	54.8
RHF/6-31G	193.795 45	56.5
RHF/6-311G	193.829 37	57.2
RHF/6-31G*	193.862 79	58.7
RHF/6-31G**	193.877 47	58.1
RHF/6-311G**//RHF/6-31G**	193.912 50	58.5
RMP2/STO-3G	192.818 33	50.1
RMP2/3-21G	193.270 41	39.3
RMP2/6-31G	194.272 44	40.1
RMP2/6-311G	194.418 26	37.7
RMP2/6-31G*	194.555 27	37.7
RMP2/6-31G**//RMP2/6-31G*	194.597 53[a]	36.5
RMP2/6-311G**//RMP2/6-31G*	194.665 70[a]	34.1
RMP2/3-21G//RMP2/6-31G*	193.261 43[a]	39.4
RMP3/3-21G//RMP2/6-31G*	193.287 66[a]	44.6
RMP4(SDTQ)/3-21G//RMP2/6-31G*	193.320 57[a]	42.1
RMP2/6-31G*	194.531 27[a]	37.7
RMP3/6-31G*//RMP2/6-31G*	194.561 88[a]	44.7
RMP4(SDTQ)/6-31G*//RMP2/6-31G*	194.602 67[a]	41.1
ΔH^{b} (RHF/3-21G, T = 200 °C)[12]	−3.6 kcal/mol	
$\Delta S^{\ddagger}$ (RHF/3-21G, T = 200 °C)[12]	−9.3 eu	
exptl $\Delta H^{\ddagger}$ (T = 200 °C)[8]	35.2 ± 2.2 kcal/mol	
exptl $\Delta S^{\ddagger}$ (T = 200 °C)[8]	−9.5 ± 4.6 eu	

[a] MP calculations used the frozen core approximation. [b] ZPE and finite temperature correction.

at 58–59 kcal/mol. Thus the HF limit gives an activation energy which is about 25 kcal/mol too high for this reaction. Inclusion of correlation energy, even at the RMP2 level with the 3-21G basis set, gives an activation energy close to the experimental value. Further improvement of the basis set at the RMP2 level (from 3-21G to 6-311G**) lowers the calculated ΔE to 34.1 kcal/mol, which, when corrected for zero-point energy and finite temperature, is significantly below the experimental result. MP2 often overestimates the effect of electron correlation on activation energies. Inclusion of more terms in the perturbation expansion (RMP3 and RMP4) results in oscillations in the ΔE, which appears to be converging around 42 kcal/mol with the 6-31G* basis. As judged from the MP2 and MP4 results with the 6-31G* and 6-311G** basis sets, the activation energy with the 6-311G** basis would probably be ~3 kcal/mol lower than with the 6-31G* basis. We estimate that the activation energy at infinite order MP with the 6-311G** basis would be approximately 39 kcal/mol. When corrected for ZPE and finite temperature using RHF/3-21G frequencies[12] scaled by a factor of 0.89,[13] this is within experimental uncertainty of the observed value of 35.2 kcal/mol. The calculated $\Delta S^{\ddagger}$ is also in good agreement with the experimental value. The isotope effect calculated for this reaction at the RHF/3-21G level is 2.52,[3b] which is in poor agreement with the experimental result of 4.97.[8a] The isotope effects are calculated from harmonic vibrational frequencies and the molecular geometry. Although improvement is expected with more accurate frequencies, it is currently impractical to calculate the frequencies at a correlated level. These high-level quantum mechanical calculations and classical transition state theory are able to account quite accurately for the observed activation parameters for this typical pericyclic reaction.

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Generation of Oxoiron(IV) Porphyrin Complexes by Amine *N*-Oxide Oxo-Transfer Reactions

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Oxoiron(IV) porphyrin prosthetic groups are now recognized as intermediates for peroxidase enzymes,[1] and such high-valent states are also suggested for cytochrome P-450[2] and cytochrome oxidase.[3] Synthetic iron(IV) porphyrin compounds have been prepared in situ at low temperature by indirect autoxidation,[4] by use of chemical oxidants,[5] by electrochemical oxidation,[6] and by photodissociation reactions.[7] Proton NMR spectroscopy has provided the major method for characterization of the iron(IV) porphyrins in solution.[4a–c,f,5]

Bruice and co-workers have investigated the kinetics and mechanism of a novel iron(III) porphyrin mediated *N*-demethylation reaction of *N*,*N*-dimethylaniline *N*-oxide.[8] Evidence favors

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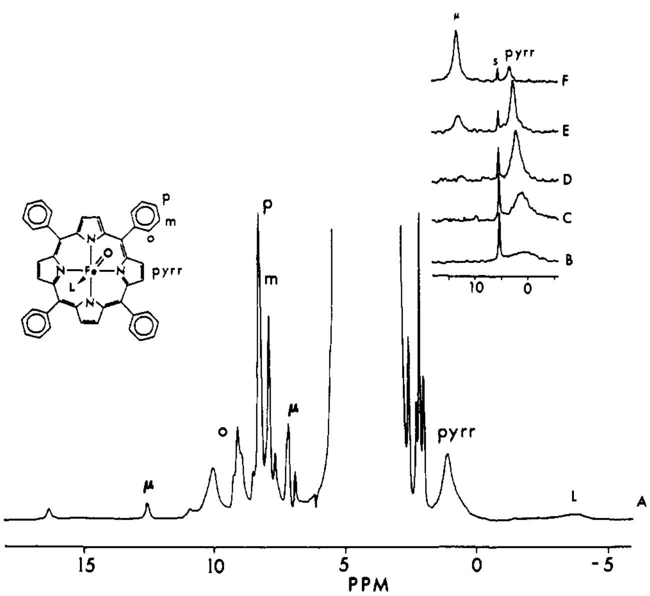

Figure 1. NMR spectra of (TPP)Fe oxidized by excess *N*-methylmorpholine *N*-oxide, dichloromethane solution; signals referenced to $(CH_3)_4Si$; μ represents signals for the dimeric (μ-oxo)iron(**III**) porphyrin byproduct; "S" is the solvent signal. (A) Proton NMR spectrum, −76 °C; (B–F) deuterium NMR spectra of the (d_8-pyrrole-TPP)Fe oxidation product; (B) −76 °C; (C) −60 °C; (D) −42 °C; (E) −26 °C; (F) −9 °C. Increased line widths at the lowest temperatures are presumably due to increased solvent viscosity and more efficient quadrupolar broadening.

initial oxo group transfer from the amine *N*-oxide to the iron(III) porphyrin catalyst with subsequent oxidative *N*-demethylation of the *N*,*N*-dimethylaniline product. Hirobe and co-workers have also reported that iron(II) porphyrins serve to deoxygenate tertiary amine *N*-oxide compounds.[9] We have studied the reaction of trialkylamine *N*-oxides with iron(II) tetraarylporphyrins at low temperature and have detected a reactive product identifiable by NMR spectroscopy as an oxoiron(IV) porphyrin. This reaction constitutes a convenient route for the in situ generation of the oxoiron(IV) porphyrin complex and also serves to demonstrate that amine *N*-oxides may perform two-electron, oxo-transfer oxidations.[10]

Crystalline square-planar iron(II) tetraphenylporphyrin ((TPP)Fe) was prepared by zinc amalgam reduction of the chloroiron(III) complex.[11] Under anaerobic conditions a 1 mM dichloromethane-d_2 solution of this species in an NMR tube at −78 °C was treated with an excess of the *N*-methylmorpholine *N*-oxide (NMNO). The resulting red solution elicited the low-temperature NMR spectra shown in Figure 1. Spectra do not match those for any known iron(II) or iron(III) tetraphenylporphyrin spin or ligation state but are reminiscent of the spectrum for the (1-methylimidazole)oxoiron(IV) tetraphenylporphyrin compound described by Chin, La Mar, and Balch.[4c] Identity of the pyrrole proton signal at 1.1 ppm for the −76 °C spectrum of the newly formed complex was confirmed by deuterium NMR examination of the analogous pyrrole-deuteriated (TPP)Fe compound. Variable-temperature deuterium NMR spectra in Figure 1 reveal approximate Curie law behavior for the pyrrole deuteron signal with a T^{-1} intercept of 10.5 ppm. The spectra also demonstrate that reduction to the dimeric (μ-oxo)iron(III) complex, (TPP)Fe–O–Fe(TPP), is apparent at −26 °C. At −9 °C the half-life for conversion to the dimeric (μ-oxo)iron(III) species is on the order of minutes. At −78 °C the newly formed complex is not sensitive to exposure to moist air, unlike the case for the precursor iron(II) porphyrin that readily takes up oxygen at low temperature. Excess amine *N*-oxide did not serve to oxidize the iron porphyrin further to the π-cation radical state. In addition, the chloroiron(III) tetraphenylporphyrin was not oxidized by either trimethylamine *N*-oxide or NMNO, but coordination of NMNO to the iron(III) center was evident on the basis of the proton NMR spectrum. The $(TPP)Fe^{II}$ derivative was not oxidized by 4-picoline *N*-oxide.

Proton NMR signals for the porphyrin phenyl groups of the newly formed complex are seen downfield of the usual aromatic region.[12] The phenyl moieties lie nearly orthogonal to the porphyrin ring, and hence splitting of the ortho and meta phenyl signals is indicative of nonequivalent occupation of axial ligand positions. This suggests that the new, putative oxoiron(IV) porphyrin could be either a five-coordinate (TPP)FeO species or could bear a second axial ligand from the excess NMNO oxidant or the free amine product. The six-coordinate structure is clearly favored for the analogous trimethylamine *N*-oxide oxidation product, as a broad signal at −30.3 ppm for a single coordinated trimethylamine *N*-oxide or trimethylamine ligand is detectable at −76 °C. No signal is seen in this far upfield region for the NMNO oxidation product, but broad signals are seen at −3.5 and −7,7 ppm (ligand orientation could drastically affect the degree of unpaired spin distribution to the axial ligand). Porphyrin signals for the trimethylamine *N*-oxide oxidation product are identical with those shown in Figure 1 for the NMNO product. Thus, a common ligation state is suggested for both complexes.

Solution magnetic moment determinations were made by the NMR method[13] between −76 and −30 °C, and corrections were applied for the small amount of dimeric (μ-oxo)iron(III) impurity. A value of $2.8 \pm 0.1\ \mu_B$ is consistent with a "spin-only" $S = 1$ state and assignment of a low-spin iron(IV) porphyrin configuration. An electron spin resonance scan at −180 °C revealed only minor signals for a high-spin iron(III) impurity. Absence of signals for the amine *N*-oxide oxidized complex is expected, given the even-spin $S = 1$ assignment.

With addition of excess 1-methylimidazole at dry ice temperature, the putative oxoiron(IV) amine *N*-oxide oxidation product is converted to the previously characterized[4a,c] (TPP)Fe(O)(1-methylimidazole) derivative. Identical pyrrole deuteron signals are seen at 2.3 ppm (−56 °C) in dichloromethane solution for this product and for the product formed by reaction of 1-methylimidazole with (TPP)Fe–O–O–Fe(TPP) (in toluene solution the signal is detected at 5.05 ppm at −80 °C[4a,c]). Addition of trimethylamine *N*-oxide or NMNO to (TPP)Fe–O–O–Fe(TPP) at −78 °C likewise serves to cleave the peroxo linkage to yield an iron(IV) porphyrin derivative with a pyrrole deuteron signal at 2.3 ppm. The far upfield resonance is absent for the (TPP)Fe–O–O–Fe(TPP)–trimethylamine *N*-oxide reaction product, and this would imply that the −30.0 ppm signal associated with the (TPP)Fe(II)–trimethylamine *N*-oxide oxidation is due to a liberated trimethylamine ligand.

The oxygen atom transfer ability of the iron(IV) porphyrin complex generated from $(TPP)Fe^{II}$ and amine *N*-oxides was demonstrated through introduction of triphenylphosphine into the reaction mixture at −56 °C. Formation of triphenylphosphine oxide was monitored over a period of hours with ^{31}P NMR spectroscopy. In the presence of excess amine *N*-oxide, approximately 10 equiv (with respect to the iron porphyrin) of triphenylphosphine was converted to the oxide. No direct oxidation of triphenylphosphine by the amine *N*-oxide was detectable under these conditions, and hence the oxygen atom transfer must be mediated by the oxidized iron porphyrin catalyst.

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In summary, a straightforward route is offered for in situ generation of oxoiron(IV) porphyrin compounds, and the direct oxo transfer chemistry for trialkylamine *N*-oxide oxidation of iron(II) porphyrins is demonstrated. Further characterization of the coordination and redox chemistry of trialkylamine *N*-oxides is in progress.

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Isolation and Structure of the Novel Dirhodium(II) Compound $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ with Bridging Bis(dimethylphosphino)methane and Ortho-Metalated Triphenylphosphine Ligands

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The preparation[1-3] and electronic structure[4] of binuclear rhodium(II) complexes possessing a Rh–Rh single bond have been topics of considerable interest in recent years. Much of the research that has been conducted in these areas focuses upon the spectral and chemical properties of the dirhodium tetracarboxylate compounds, species which form axial adducts with a wide variety of σ-donor and π-acid ligands. The metathesis reactions of the bridging carboxylate groups have been well-investigated. For example, the acetate groups in $Rh_2(\mu\text{-}O_2CCH_3)_4L_2$ can be replaced by other $R'CO_2^-$ groups or by a variety of different ligands such as sulfate,[5] dihydrogenphosphate,[6] amidate,[7] or 2-oxypyridine anions.[2] Quite often, the products isolated from these reactions contain four bridging ligands of the same type, viz., $[Rh_2(SO_4)_4(H_2O)_2]^{4-}$, $Rh_2(H_2PO_4)_4(H_2O)_2$, $Rh_2(HNOCCH_3)_4(H_2O)_2$, and $Rh_2(mhp)_4$ (mhp = 2-methylhydroxypyridinato).

Among the few documented examples of dirhodium(II) compounds containing more than one kind of bridging groups are the structurally characterized compounds $Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2{\cdot}C_7H_8$[8] and $Rh_2(O_2CCH_3)_2(mhp)_2(Im)$[9] and the amidato–carboxylato complexes reported by Bear et al.[7] Several additional mixed-ligand $Rh^{II}Rh^{II}$ compounds of an unusual type were recently prepared in our laboratories from the reactions of $Rh_2(\mu\text{-}O_2CCH_3)_4$ with tertiary arylphosphines. When the phosphine $P(O\text{-}BrC_6F_4)Ph_2$ (PCBr) was used, four major products were formed, each of which possesses several $\mu\text{-}O_2CCH_3$ groups and at least one ortho-metalated PCBr ligand,[10,11] An earlier study of the reaction between PPh_3 and $Rh_2(O_2CCH_3)_4$ in refluxing acetic acid led to the isolation of $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2(L)_2$ (L = CH_3COOH, C_5H_5N), a molecule containing two $\mu\text{-}O_2CCH_3$ ligands in a cisoid arrangement and two bridging $o\text{-}(Ph_2P)C_6H_4^-$ anions,[12] It is the reactivity of this ortho-metalated compound which is the topic of the present communication,

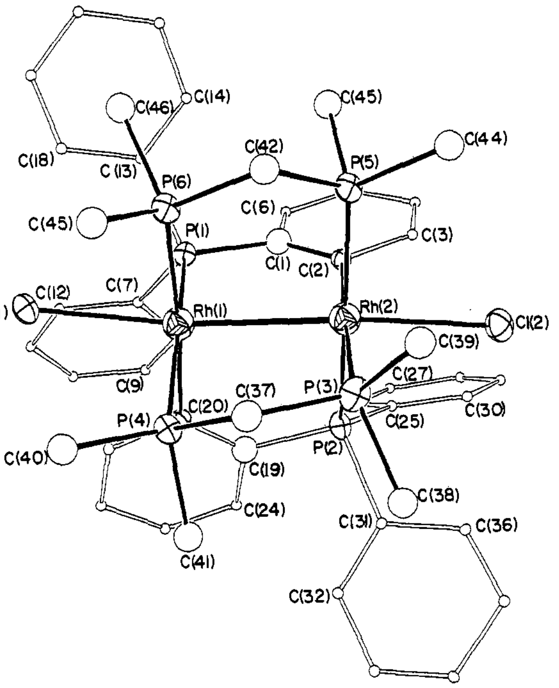

Figure 1. ORTEP drawing of the $Rh_2(dmpm)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ molecule with the atom labeling scheme. Some important distances (Å) and angles (deg): Rh(1)–Rh(2), 2.770 (3); Rh(1)–Cl(1), 2.561 (6); Rh(2)–Cl(2), 2.527 (6); Rh(1)–P(1), 2.345 (6); Rh(1)–P(4), 2.302 (6); Rh(1)–C(20), 2.07 (2); Rh(2)–C(2), 2.09 (2); P(1)–C(1), 1.80 (2); P(1)–C(7), 1.89 (2); P(4)–C(37), 1.82 (2); P(4)–C(40), 1.83 (2); C(1)–C(2), 1.41 (3); C(7)–C(8), 1.40 (3); Rh(2)–Rh(1)–Cl(1), 172.5; Rh(2)–Rh(1)–P(1), 89.0 (2); Rh(2)–Rh(1)–P(4), 91.1 (2); Rh(2)–Rh(1)–C(20), 90.1 (6); Cl(1)–Rh(1)–P(1), 91.8 (2); Cl(1)–Rh(1)–P(4), 89.7 (2); Cl(1)–Rh(1)–C(20), 97.4 (6); P(1)–Rh(1)–P(4), 167.4 (2); Rh(1)–Rh(2)–Cl(2), 171.4 (1); P(3)–C(37)–P(4), 106 (1).

We have found that the acetate ligands in $Rh_2(O_2CCH_3)_2(PPh_2C_6H_4)_2$ and also in $Rh_2(O_2CCH_3)_4$[13] can be labilized by using trimethylsilyl chloride. This synthetic approach was first reported by McCarley and co-workers[14] and by Green et al.,[15] who found that $SiMe_3Cl$ acts as a mild and selective reagent for the replacement of μ-acetato groups in $Mo_2(O_2CCH_3)_4$.

For the past several years, we have endeavored to demonstrate the general utility of this type of reaction as a method for the high-yield synthesis of new bimetallic compounds of Mo,[16] W,[17]

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